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Supplementary Materials: Ammonia Generation via a Graphene-Coated Nickel Catalyst

Fei Lu and Gerardine G. Botte *

Center for Electrochemical Engineering Research (CEER), Chemical and Biomolecular Engineering Department, Ohio University, Columbus, OH 43210, USA; fl150709@ohio.edu

* Correspondence: botte@ohio.edu; Tel.: +1-740-593-9670

S1. Determination of Produced Ammonia Using Ion Selective Electrode

The generated ammonia in the experiments was determined using an ammonia ion selective electrode (ISE) (Thermo 710A+, measurement error is ± 2%). The ammonia ISE was calibrated by 0.121, 1.21, 12.1, 121 ppm as ammonia standard solutions (1 ppm = 5.87×10^{-5} M), made by dilution from 1000 ppm as nitrogen standard (Thermo Scientific, Orion 951007). At each sample point, 0.5 mL electrolyte sampled from the reactor was diluted to 100 ml. The ammonia concentration in the diluted samples was then determined by ammonia ISE. The concentration and the amount of ammonia in the reactor were calculated using Equations (S1) and (S2). Only ammonia in the reactor solution was measured.

$$C_{NH_3} = C_{NH_3,\,sample} \times 200 \times 5.87 \times 10^{-5} \quad \text{(S1)}$$

$$n_{NH_3} = C_{NH_3} \cdot V_{reactor} \quad \text{(S2)}$$

where: $C_{NH3,sample}$, concentration of ammonia in the diluted sample measured by ammonia ISE, ppm; C_{NH3}, concentration of generated ammonia in the reactor, M; n_{NH3}, amount of the generated ammonia in the reactor, mol; $V_{reactor}$, volume of the electrolyte in the reactor, L, $V_{reactor}$ = 0.1251.

S2. Determination of Ni Loss Using Atomic Absorption Spectrometry

Atomic absorption spectrometry (AAS) was used to determine the concentration of Ni ions in the reagent solution during the experiments in the eU2A reactor. The atomic absorption spectrometer (AAnalyst 400, PerkinElmer, Inc., Waltham, MA, USA) used air-acetylene flame as the atomizer and Ni hollow cathode lamp (232 nm) as the radiation source for AAS measurement. Standard solutions of 2 ppm to 12 ppm were prepared by dilution from 1000 ppm Ni reference standard solution (FLSN70-500, ±1%, Fisher Scientific). The nonlinear regression curve of absorbance for 2 to 12 ppm standard Ni ion solutions is shown in Figure S1a. At each sample point, 0.5 mL electrolyte sampled from the reactor was diluted to 10 ml as testing samples. The concentrations of Ni ions in the testing samples were given after calibration with the standard solutions, and the concentration of Ni ions in the electrolyte was then calculated using Equation (S3) and plotted in Figure S1b. Because the geometric areas of the working electrodes (graphene-coated Ni and bare Ni) are different, the normalized concentration of Ni ions in the electrolyte was calculated by Equation (S4) and shown in Figure 8a.

$$C_{Ni\ ion} = C_{Ni\ ion\ sample} \times 20 \quad \text{(S3)}$$

$$\overline{C}_{Ni\ ion} = \frac{C_{Ni\ ion}}{A} \quad \text{(S4)}$$

where, $C_{Ni\ ion\ sapmle}$, concentration of Ni ion in the diluted testing samples, mg L^{-1}; $C_{Ni\ ion}$, concentration of Ni ion in the electrolyte during the experiments, mg L^{-1}; $\overline{C}_{Ni\ ion}$, normalized concentration of Ni ion in the electrolyte, mg L^{-1} cm^{-2}; A, geometric area of the working electrode, cm^2.

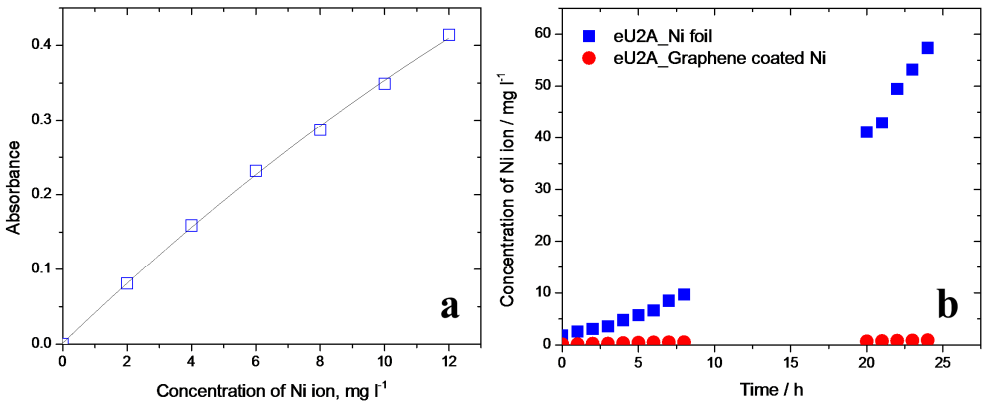

Figure S1. (**a**) Calibration curve of standard Ni^{2+} solutions with concentrations from 2 to 12 ppm for AAS measurement; (**b**) Concentration of Ni ion in the electrolyte during 24 h eU2A experiments using Ni foil and graphene-coated Ni working electrode.

S3. Scanning Electron Microscopy

The graphene-coated Ni electrode was characterized by scanning electron microscopy (SEM) using a JEOL JSM-6390 scanning electron microscope (15kV, 14 mm working distance). The images were obtained before masking the edge of graphene on Ni substrate for eU2A experiments. The morphology of the samples shows that graphene is homogenously covered on the Ni substrate with small defects.

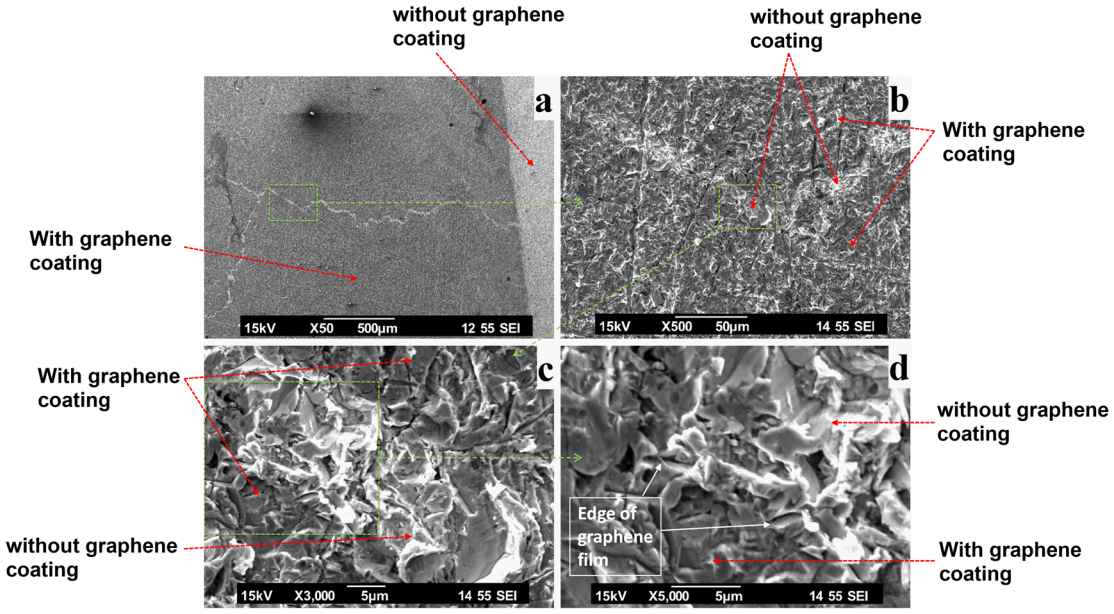

Figure S2. SEMs of the graphene-coated Ni with magnification of (**a**) 50, (**b**) 500, (**c**) 3000, and (**d**) 5000. The area highlighted with a green rectangle corresponds to the higher magnification on the next image pointed out by a green arrow.